Molecular Dynamics Study of Water Vapor Adsorption into Ordered Mesoprous Silica

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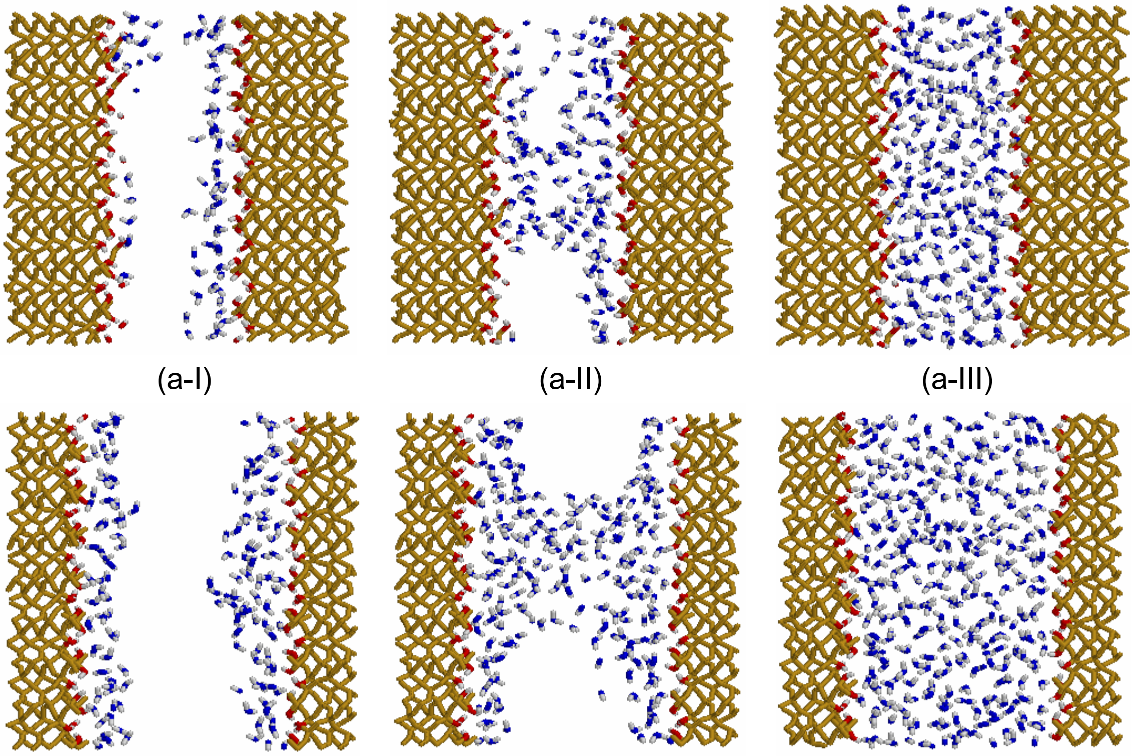
Microporous and mesoporous materials have been applied as adsorbents. The knowledge of the structural and dynamical properties of adsorbates is essential for the design of adsorbents, but the properties of adsorbates have not yet been clarified. In our previous study [1], the properties of water molecules in zeolites NaX (Si/Al = 1.0) and NaY (Si/Al = 2.0) were investigated with molecular dynamics (MD) simulations. The calculation results show that in zeolite NaX, the water vapor adsorption can be expressed by using the Langmuir model with two adsorption sites, but in zeolite NaY, it is not Langmuir-type adsorption. In this study, the MD simulations of hydrated ordered mesoporous silicas were performed. Despite the several previous studies [2-5], the adsorption phenomena inside the ordered mesoporous silicas have not yet been clarified on the molecular level. The objective of this study is to clarify the structural and dynamical properties of water molecule inside the ordered mesoporous silicas and to obtain the molecular pictures of the adsorption process.

The dimension of calculation cell is 4.422 x 4.255 x 4.324 nm^3, that is, 720 orthorhombic unit cell of α-quartz (Si_3O_6), and a pore of about 2.0/2.8 nm in diameter and 4.324 nm in height was made in the α-quartz crystal. The surface densities of SiOH groups inside pores of 2.0 and 2.8 nm in diameter were 7.07 and 7.49/nm^2, respectively. For the potential functions, the Tsuneyuki model [7] was employed for SiO_2 molecules. The SiOH groups were regarded as rigid body and the charge of H atom of SiOH group was determined to neutralize the whole systems electrically. The water molecules were assumed to interact via the SPC/E potential. The potential between water-mesoporous silicas involved two contributions: a Coulomb interaction between all the atoms and a Born-Mayer-Huggins (BMH) interaction between the oxygen atoms of water (OW) and the oxygen atoms of mesoporous silicas (OM). In the calculation of the BMH parameters between OW and OM, the combination rule used in the Tsuneyuki model was employed. Initially, dehydrated mesoporous silicas were equilibrated by MD calculation. After the equilibration, water molecules were distributed at random inside the pore, and then the simulations of hydrate mesoporous silicas were performed in NVT ensemble. The number of water molecules for 2.0 and 2.8 nm diameter pores were 0, 48, 96, 144, 192, 240, 288 and 0, 96, 192, 288, 384, 480, 576, 624, 672, respectively. The 3-dimentional periodic boundary condition was applied in the calculation cell and the simulations were run for about 1 ns after equilibration. The atomic positions were output every 200 fs.

The calculated adsorption structures are shown in fig. 1. At low hydration ($N \leq 96$ for 2.0 nm diameter pore; $N \leq 384$ for 2.8 nm diameter pore), water molecules adsorbed on the surface and the adsorption layers were formed. [Figures 1a-I and b-I]. At intermediate hydration ($128 < N < 288$ for 2.0 nm diameter pore; $384 < N < 624$ for 2.8 nm diameter pore), the

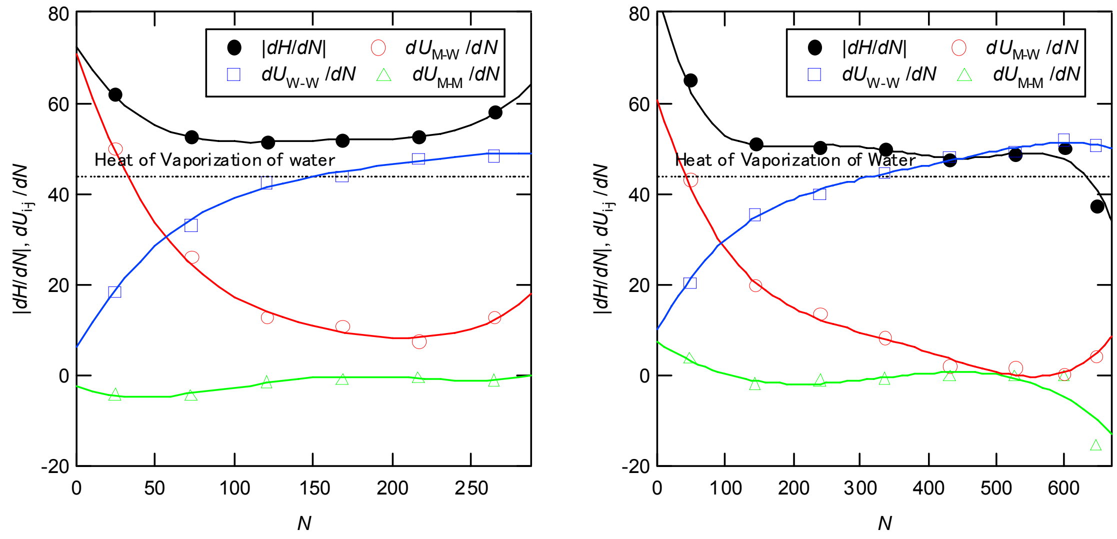

(a-I) (a-II) (a-III)

(b-I) (b-II) (b-III)

Fig. 1 Snapshots of water distribution in a cross-section of two different diameter mesoporous silicas with different numbers of water molecules: (a-I) N = 48, (a-II) N = 144 and (a-III) N = 288 for a mesoporous silica with 2.0 nm in diameter, and (b-I) N = 384, (b-II) N = 480 and (b-III) N = 624 for a mesoporous silica with 2.8 nm in diameter. The water molecules were depicted only within the thickness of 10.0 Å.

water molecules condensed inside pores [Figures 1a-II and b-II]. At high hydration ($N \geq 288$ for 2.0 nm diameter pore; $N \geq 624$ for 2.0 nm diameter pore), pores were filled with water molecules [Figures 1a-III and b-III]. These snapshots suggest that water molecules adsorb on the surface at low hydration, but the adsorption on the surface and the condensation inside the pore occur simultaneously at intermediate hydration.

To evaluate the interaction energy, the differential heats of adsorption were investigated. The differential heat of adsorption, j*dH/dN*j, is defined as $|dH/dN|=|dU/dN+RT|$. where dU/dN is the derivative of the potential energy with respect to the number of water molecules, and R and T are gas constant and temperature, respectively. The potential energy of a unit cell, U, can be decomposed into three terms: the potential energies between mesoporous silica-water, water-water, and mesoporous silica-mesoporous silica, $U_{\text{M-W}}$, $U_{\text{W-W}}$, $U_{\text{M-M}}$. The derivatives of the potential energy with respect to the number of water molecules, dU/dN, can also be decomposed as $dU/dN = dU_{\text{M-W}}/dN + dU_{\text{W-W}}/dN + dU_{\text{M-M}}/dN$. Figures 2a and 2b show the differential heat adsorption and the negatives of three decomposed terms



(a) (b)

Fig.2 Differential heats of adsorption, |*dH*/*dN*|, and negatives of differential potential energies between mesoporous silica-water, water-water, and mesoporous silica-mesoporous silica, $-dU_{\mathrm{M\text{-}W}}/dN$, $-dU_{\mathrm{W\text{-}W}}/dN$, and $-dU_{\mathrm{M\text{-}M}}/dN$ for mesoporous silicas of (a) 2.0 nm and (b) 2.8 nm in diameter. Lines and points were obtained from polynomial and linear interpolation, respectively. *N* is the number of water molecules. Relevancy of these values is expressed by $|dH/dN| = -dU_{\mathrm{M\text{-}W}}/dN -dU_{\mathrm{W\text{-}W}}/dN - dU_{\mathrm{M\text{-}M}}/dN - RT$. *RT* is 2.494 kJ/mol at 300 K.

for mesoporous silicas of 2.0 and 2.8 nm in diameter, respectively. The calculated differential heats of adsorption agree with the measured values. At low hydration, the interaction energies between mesoporous silica-water, $-dU_{\mathrm{M\text{-}W}}/dN$, decrease from about 60 kJ/mol to less than 15 kJ/mol and the interaction energies between water-water, $-dU_{\mathrm{W\text{-}W}}/dN$, increase from 20 kJ/mol to the value of the heat of vaporization of water. After intermediate hydration states ($N > 96$ for 2.0 nm diameter pore; $N > 384$ for 2.8 nm diameter pore), $-dU_{\mathrm{M\text{-}W}}/dN$ are almost the same to the heat of vaporization of water. These features of adsorption heat can be related to the adsorption structures in fig. 1. At initial adsorption, water molecules make adsorption layer on the wall while $-dU_{\mathrm{M\text{-}W}}/dN$ decrease. After intermediate hydration state, water molecules condense in pores and major changes cannot be seen in differential potential energies. This calculation result suggests that although the total differential heats of adsorption except for extremely low hydration state are almost constant for both types of mesoporous silicas, the adsorption mechanism varies with the hydration states.

[References]

(1) K. Shirono, A. Endo and H. Daiguji, *J. Phys. Chem. B* 2005, **109**, 3446.
(2) E. Spohr, C. Hartnig, P. Gallo, and M. Rovere, *J. Mol. Liq.* 1999, **80**, 165.
(3) P. Gallo, M. A. Ricci, and M. Rovere, *J. Chem. Phys.* 2002, **116**, 342.
(4) J. Puibasset and R. J.-M. Pellenqz *Phys. Chem. Chem. Phys.* 2004, **6**, 1933.
(5) D. A. Litton and S. H. Garofalini, *J. Appl. Phys.* 2001, **89**, 6013.
(6) S. Tsuneyuki, M. Tsukada, H. Aoki and Y. Matsui *Phys. Rev. Lett.* 1988, **61**, 869.